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## (54) REDUCTIVE DECOMPOSITION OF OXIDES OF NITROGEN

(71) We, MITSUBISHI CHEMICAL INDUSTRIES LTD., a Japanese Company, of 5-2, Marunouchi 2-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to the reductive decomposition of oxides of nitrogen. More particularly, the invention relates to an improvement in the catalytic reduction of oxides of nitrogen e.g.  $\text{N}_2\text{O}$ ,  $\text{NO}_2$  (hereinafter referred to as  $\text{NO}_x$ ) in exhaust gases in the presence of ammonia.

Oxides of nitrogen ( $\text{NO}_x$ ) are toxic to the human body. When  $\text{NO}_x$  is absorbed by the human body, body functions begin to decrease. There is a great need for efficient methods of removing  $\text{NO}_x$ , also because  $\text{NO}_x$  causes a photochemical smog which is described as oxidative.

Accordingly, it is a most important problem to remove  $\text{NO}_x$  in the exhaust gases from polluting sources such as power plants, nitric acid plants, automobiles and the like.

Hitherto, various methods for removing  $\text{NO}_x$  have been proposed. In known methods, the reductive decomposition method using ammonia as a reducing agent is effective in treating exhaust gas containing relatively high concentrations of  $\text{NO}$  and  $\text{O}_2$ .

In a known practical method, the exhaust gas has been contacted with a vanadium oxide catalyst.

However, when the vanadium oxide catalyst prepared by immersing a known carrier in an aqueous solution of a vanadium salt and calcining the product, is used and  $\text{NO}_x$  in the gas is reduced and decomposed in the presence of ammonia, the catalytic activity has not been satisfactory and also the optimum temperature range has been limited. The present invention has been attained after long studies for overcoming these difficulties.

It is an object of the present invention to provide process for the catalytic reductive decomposition of oxides of nitrogen with high catalytic activity.

In accordance with the invention there is provided a process for the reductive decomposition of oxides of nitrogen contained in a gas which comprises treating the gas with ammonia in the presence of a catalyst comprising as active ingredients vanadium oxide supported on a carrier formed at least externally of titanium oxide, zirconium oxide, cerium oxide,  $\gamma$ -alumina, or a mixture of two or more thereof.

The catalyst may be prepared by dipping the carrier in an aqueous solution of a vanadium compound and calcining it at 400-700°C.

Exhaust gas containing  $\text{NO}_x$  treated by the method of the invention can be any exhaust gas discharged from polluting sources such as power plants, nitric acid plants, automobile engines, and the like.

Usually exhaust gases contain more than 0.1 vol. % oxygen, especially 2-10 vol. % oxygen, together with  $\text{NO}_x$ .

It is usual to feed ammonia at a molar ratio of 0.5 or more preferably 0.5-2 with respect to  $\text{NO}_x$  in the exhaust gas. When the molar ratio of ammonia to  $\text{NO}_x$  is too low, a desirable  $\text{NO}_x$  decomposition is not obtained.

When the molar ratio of ammonia to  $\text{NO}_x$  is too high, it is not economical and the unreacted ammonia is included in the exhaust gas. One form of catalyst comprises vanadium oxide supported on a carrier comprising one or more of titanium oxide, zirconium oxide, cerium oxide and  $\gamma$ -alumina. Preferably, the carrier comprises titanium oxide, zirconium oxide or a mixture thereof. An example of the catalyst can be prepared as follows.

Vanadium pentoxide is dissolved in water with oxalic acid; or a vanadium salt such as vanadyl sulfate, vanadyl chloride or ammonium metavanadate is dissolved in water.

A moulded support of titanium oxide, zirconium oxide or the mixture thereof is dipped in the aqueous solution for several hours and then dried and calcined.

Powdered titanium oxide or zirconium oxide may be dipped in the aqueous solution and the wet powder extruded to mould it, if desired after drying it or after drying and calcining it to form the oxide. The shape of the moulding can be chosen without limitation, and spherical, pellet and honeycomb shaped carriers can be used. The titanium oxide may be of the rutile type and/or the anatase type crystalline structure. The latter is especially preferable.

The vanadium oxide may be supported by the carrier in amounts ranging preferably from 0.1—50% by weight especially 1—20% by weight to total weight of the catalyst. Another form of catalyst used in the invention comprises vanadium oxide supported on a heat resisting substance coated with titanium oxide. Any heat resistant substance can be used for the preparation of the carrier, e.g. alumina, silica-alumina and also diatomaceous earth, silicon carbide, mullite, zirconia or cordierite.

The shape of the heat resistant substance can be chosen without limitation and spherical, pellet and honeycomb shaped carriers can be used.

For example, a heat resistant substance is coated with titanium oxide as follows.

The heat resistant substance is dipped in an aqueous solution of titanium tetrachloride, titanium trichloride, titanium sulfate or other titanium salt for a suitable time and is then exposed to the atmosphere, and if desired, treated with an alkaline solution and calcined at 500—600° C in air to form the titanium oxide coat by oxidizing decomposition and hydrolysis.

When titanium tetrachloride is used, the completion of the formation of titanium oxide can be confirmed by observing no further generation of white smoke. The product is washed with water at room temperature if desired, and calcined.

The heat resistant substance coated with titanium oxide can be also obtained by immersing said substance in a slurry containing titanium oxide.

Then, vanadium oxide is supported on the

resulting carrier as follows.

The carrier is dipped in an aqueous solution of one or more vanadium salts such as vanadyl oxalate, vanadyl sulfate, vanadium tetrachloride, vanadyl chloride and ammonium metavanadate, and is dried and calcined.

The vanadium oxide is supported by the carrier in amounts ranging preferably from 0.1—50% by weight, preferably 1—20% by weight as  $\text{V}_2\text{O}_5$  to total weight of the catalyst.

The heat resistant substance coated with titanium oxide may be dipped in the aqueous solution of the vanadium salt for about 1—20 hours preferably 1—5 hours.

After the impregnating treatment, the carrier may be gradually heated in air or a nitrogen atmosphere to dry it and then to calcine it at 400—700° C to give the final catalyst.

Another form of catalyst used in the invention comprises cerium oxide and vanadium oxide supported on a heat resistant substance. The heat resisting substance used for supporting the active component i.e. cerium oxide and vanadium oxide can be e.g. alumina, silica, silica-alumina, diatomaceous earth, zirconia, titania, mullite, cordierite. The heat resistant substance can be made by moulding it to the form e.g. of granules, pellets or honeycomb shape.

A catalyst to be used in the invention can be prepared by supporting cerium oxide on the heat resistant substance in the first instance.

The heat resisting substance may be dipped in an aqueous solution of one or more cerium salts such as cerium nitrate, cerium chloride, cerium sulfate and cerium ammonium nitrate, and is taken up and it is gradually heated in air or a nitrogen atmosphere to dry it and then to calcine it at 400—700° C.

The cerium oxide may be supported by the heat resistant substance in amounts ranging from 0.1—20% by weight preferably 1—10% by weight as  $\text{CeO}_2$  based on the total weight of the catalyst.

After such treatment, vanadium oxide is preferably supported as follows.

The carrier made of the heat resistant substance supporting cerium oxide is dipped in an aqueous solution of one or more vanadium salts such as vanadyl oxalate, vanadyl sulfate, vanadyl tetrachloride, ammonium metavanadate and is taken up, and it is gradually heated in air or a nitrogen atmosphere to dry it and then to calcine it at 400—700° C to give the catalyst.

The vanadium oxide may be supported by the carrier in amounts ranging 0.1—30% by weight, preferably 1—10% by weight as  $\text{V}_2\text{O}_5$  to total weight of the catalyst.

Another form of catalyst used in the invention comprises vanadium oxide supported on a carrier made of a heat resistant substance coated with  $\gamma$ -alumina.

The carrier made of the heat resistant substance coated with  $\gamma$ -alumina can be pre-

pared by any known method.

For example, a ceramic moulded substance is dipped in a slurry or colloidal solution containing  $\gamma$ -alumina or a  $\gamma$ -alumina-producing compound such as boehmite or aluminium hydroxide, and then is taken up and calcined to give the carrier.

The ceramic can be mullite, cordierite,  $\alpha$ -alumina, etc. and is moulded to form any desired shape.

Although the shape is not limited, it is especially preferable to form a honeycomb shape which has an advantage of low pressure loss even though velocity of the gas mixture of the exhaust gas being treated and ammonia gas, that is the space velocity, is high. Usually, the shape of the honeycomb can have in sectional view many hexagonal, rectangular, triangular or circular openings. A honeycomb having a sinusoidal section, or having spidery or scrolled openings can be used.

In order to support vanadium oxide as a catalytic active component on the carrier, the carrier may be dipped in an aqueous solution of vanadyl oxalate, vanadyl sulfate, vanadyl chloride, ammonium metavanadate for e.g. several hours and then is dried and calcined.

The vanadium oxide may be supported by the carrier in amounts ranging 0.1—50% by weight preferably 1—20% by weight as  $V_2O_5$  to total weight of the catalyst.

Another form of catalyst used in the invention comprises vanadium oxide supported on a carrier made of a heat resistance substance coated with a mixture of titanium oxide and  $\gamma$ -alumina.

In order to perform the reductive decomposition of  $NO_x$  in the exhaust gas by using a catalyst prepared as above, it is quite effective to pass the exhaust gas through the catalyst zone at a space velocity of 1,000—150,000  $hr^{-1}$ , preferably 10,000—100,000  $hr^{-1}$  at a temperature of 150—650° C preferably 200—500° C. The reductive decomposition products are mostly nitrogen and water.

When the reductive decomposition of  $NO_x$  is performed in the presence of ammonia by using the catalyst prepared as above, the catalytic activity is remarkably higher than that using a known catalyst. The high catalytic activity is maintained without substantial change of activity, even though the temperature is changed. Accordingly, the method of the invention is advantageous in practical operation. The invention will be illustrated by certain Examples. In the Examples, the catalytic activity tests are conducted as follows.

A gas containing 10 vol. % of oxygen, 2000 ppm of  $NO_x$  ( $NO_2$  300 ppm) and 3000 ppm of  $NH_3$  was passed through the catalyst layer at a space velocity of 40,000  $hr^{-1}$  in the case of a honeycomb type catalyst; and at space

velocity of 20,000  $hr^{-1}$  in the case of other types of catalyst, at a predetermined temperature. The concentration of  $NO_x$  was measured before and after the addition of ammonia, and the  $NO_x$  removal ratio (%) is given by the equation.

$$NO_x \text{ removal ratio (\%)} = \frac{[NO_x(\text{inlet}) - NO_x(\text{outlet})]/[NO_x(\text{inlet})] \times 100}{}$$

The concentration of  $NO_x$  was measured by the chemiluminescent  $NO_x$  analyzer (CLM—201 manufactured by Shimadzu-Seisakusho K.K.).

#### Example 1.

Powdered titanium oxide (anatase type, surface area of 36  $m^2/gr$ ) was moulded to form tablets having diameter of 8 mm and thickness of 2 mm. 10 ml of the tablets were immersed for an hour in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 3.58 g of vanadium pentoxide and 8.24 g of oxalic acid, and the solution was filtered off and the residual tablets were dried and calcined at 250° C for 1 hour, at 350° C for 1 hour and then at 500° C for 3 hours in an air stream to yield a catalyst of titanium oxide supporting 10% by weight of vanadium oxide.

The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 1.

#### Example 2.

Powdered titanium oxide (rutile type, surface area of 8.5  $m^2/gr$ ) was moulded to form tablets having diameter of 8 mm and thickness of 2 mm. 10 ml of the tablets were immersed for an hour in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 4.96 g vanadium pentoxide and 11.4 g of oxalic acid, and the solution was filtered off and the residual tablets were dried and calcined in accordance with the process of Example 1, to yield a catalyst of titanium oxide supporting 10% by weight of vanadium oxide.

The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 1.

#### Example 3.

Powdered titanium oxide (rutile type, surface area of 6.8  $m^2/gr$ ) was moulded to form tablets having diameter of 8 mm and thickness of 2 mm. 10 ml of the tablets were immersed for an hour in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 5.29 g of vanadium pentoxide and 12.17 g of oxalic acid, and the solution was filtered off and the residual tablets were dried and calcined in accordance with the process of Example 1, to yield a catalyst of titanium oxide supporting 10% by weight of vanadium oxide.

The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 1.

TABLE 1

Example	Amount of $V_2O_5$ supported (wt. %)	Amount of catalyst (g)	Reaction temperature ( $^{\circ}C$ )	$NO_x$ removal ratio (%)
1	10	9.9	200	67
			240	80
			280	90
			320	94
			340	95.5
			370	95.5
			400	91.5
2	10	11.8	420	81
			250	64
			300	79
			340	86
			380	89.5
			400	89.5
3	10	12.4	420	85
			280	58
			320	68
			360	74
			400	75.5
			420	73

## Example 4.

A 15 g of powdered zirconia was immersed in 5 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 1.67 g of vanadium pentoxide and 3.83 g of oxalic acid, and the mixture was concentrated and dried, and then calcined at 500° C for 30 minutes

and the product was moulded to form tablets having diameter of 8 mm and thickness of 2 mm.

A catalyst of zirconia supporting 10% by weight of vanadium oxide was obtained.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 2.

TABLE 2

Example	Amount of V <sub>2</sub> O <sub>5</sub> supported (wt. %)	Amount of catalyst (g)	Reaction temperature (°C)	NO <sub>x</sub> removal ratio (%)
4	10	14.7	250	69
			300	83
			340	88.5
			360	89.5
			380	89
			400	84
			420	75

## Example 5.

10 ml of γ-alumina was immersed in 10 ml of titanium tetrachloride and was taken up and oxidized by exposing it in air for several hours and then the product was washed with water for several minutes and calcined at 500° C for three hours in nitrogen atmosphere to yield γ-alumina coated with titanium oxide.

The 10 ml of γ-alumina coated with titanium oxide was immersed in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 2.22 g of vanadium pentoxide and 5.11 g of oxalic acid and the mixture was filtered.

The residual product was dried and calcined in accordance with the process of Example 1, to yield a catalyst of γ-alumina coated with titanium oxide supporting 10% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

## Example 6:

In accordance with the process of Example 5, titanium oxide was coated on γ-alumina.

The 10 ml of γ-alumina coated with titanium oxide was immersed in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 3.29 g of vanadium pentoxide and 7.56 g of oxalic acid, and the mixture was filtered and the product was calcined in accordance with the process of Example 1 to yield a catalyst of γ-alumina coated with titanium oxide supporting 5% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

## Example 7.

In accordance with the process of Example 5, titanium oxide was coated on silica.

10 ml of silica coated with titanium oxide was immersed for an hour in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 0.18 g of vanadium pentoxide and 1.81 g of oxalic acid, and the solution was filtered off and the product was calcined in accordance with the process of Example 1, to yield a catalyst of silica coated with titanium oxide supporting 5% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

## Reference Example 1.

10 ml of silica of Example 7 which is not coated with titanium oxide was immersed in an aqueous solution of vanadium salt and the product was calcined in accordance with the process of Example 7, to yield a catalyst of silica supporting 5% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

## Example 8.

In accordance with the process of Example 5, titanium oxide was coated on silica-alumina.

10 ml of silica-alumina coated with titanium oxide was immersed for an hour in 10 ml

of an aqueous solution of vanadyl oxalate prepared by dissolving 1.09 g of vanadium pentoxide and 2.50 g of oxalic acid, and the mixture was filtered and the product was calcined in accordance with the process of Example 1 to yield a catalyst of silica-alumina coated with titanium oxide supporting 5% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

#### Reference Example 2.

10 ml of silica-alumina of Example 8, which is not coated with titanium oxide was immersed in an aqueous solution of vanadium salt and the product was calcined in accordance with the process of Example 8, to yield a catalyst of silica-alumina supporting 5% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

#### Example 9.

In accordance with the process of Example 5, titanium oxide was coated on  $\alpha$ -alumina

honeycomb.

One  $\alpha$ -alumina honeycomb (about 5 ml) coated with titanium oxide was immersed for an hour in 20 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 6.02 of vanadium pentoxide and 13.83 g of oxalic acid in water, and the mixture was filtered and the product was calcined in accordance with the process of Example 1, to yield a catalyst of  $\alpha$ -alumina honeycomb coated with titanium oxide supporting 5% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

#### Reference Example 3.

The  $\alpha$ -alumina honeycomb of Example 9 which is not coated with titanium oxide was immersed in the aqueous solution of vanadium oxalate and the product was calcined in accordance with the process of Example 1, to yield a catalyst of  $\alpha$ -alumina honeycomb supporting 5% by weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using the catalyst are shown in Table 3.

TABLE 3

Example	Amount of V <sub>2</sub> O <sub>5</sub> supported (wt. %)	Amount of Catalyst (g)	Reaction temperature (°C)	NO <sub>x</sub> removal ratio (%)
5	10	7.0	200	58
			250	74
			300	86.5
			340	91
			380	93
			420	93
			440	92
			460	88
			480	81
Example 6	5	13.1	250	51
			300	67
			340	75.5
			380	80
			400	80
			420	75
			440	63

TABLE 3 (continued)

	Amount of $V_2O_5$ supported (wt. %)	Amount of Catalyst (g)	Reaction temperature (°C)	$NO_x$ removal ratio (%)
Example 7	5	5.6	280	52
			320	60
			360	62.5
			380	61.5
			400	58
Reference Example 1	5	4.8	280	17
			320	20
			360	18
			380	12
Example 8	5	7.0	250	67
			300	79
			340	87
			380	90
			420	91
			440	91
			460	90
			480	88
Reference Example 2	5	5.7	500	81
			380	59
			420	63
			460	65
			500	66
Example 9	5	5.8	540	64
			260	61
			300	73.5
			340	81
			360	83
			380	83
			410	79.5
Example 9	5	5.8	430	66

TABLE 3 (Continued)

	Amount of $V_2O_5$ supported (wt. %)	Amount of Catalyst (g)	Reaction temperature (°C)	$NO_x$ removal ratio (%)
Reference Example 3	5	5.6	270	27.5
			330	33.5
			380	36.5
			400	35

## Example 10.

- 15 ml of  $\gamma$ -alumina was immersed in 15 ml of an aqueous solution of 3.9 g cerium nitrate for 1 hour, and the solution was filtered and the product was dried and calcined at 250° C for 1 hour and at 350° C for 1 hour and at 500° C for 3 hours in nitrogen atmosphere for 3 hours to yield 15 ml of  $\gamma$ -alumina supporting cerium oxide. The 15 ml of  $\gamma$ -alumina supporting cerium oxide was immersed for an hour in 15 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 3.3 g of vanadium pentoxide and 7.7 g of oxalic acid and filtered, and the product was dried and calcined in accordance with the process of Example 1 to yield a catalyst of  $\gamma$ -alumina supporting 5% by weight of cerium oxide and 10% by weight of vanadium oxide.

- The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 4.

## Example 11.

- In accordance with the process of Example 10, cerium oxide was supported on  $\gamma$ -alumina.

- 15 ml of the  $\gamma$ -alumina supporting cerium oxide was immersed for an hour in 15 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 1.6 g of vanadium pentoxide and 3.6 g of oxalic acid and filtered and the product was dried and calcined in accordance with the process of Example 10 to yield a catalyst of  $\gamma$ -alumina supporting 5% by weight of cerium oxide and 5% by weight of vanadium oxide.

- The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 4.

## Example 12.

- 15 ml of  $\alpha$ -alumina was immersed in 15 ml of an aqueous solution of 6.9 g of cerium nitrate for 1 hour and the product was dried and calcined in accordance with the process of Example 10 to yield 15 ml of  $\alpha$ -alumina supporting cerium oxide.

- The 15 ml of  $\alpha$ -alumina supporting cerium oxide was immersed for an hour in 15 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 1.1 g of vanadium pentoxide and 2.4 g of oxalic acid and filtered and the

product was dried and calcined in accordance with the process of Example 10 to yield a catalyst of  $\alpha$ -alumina supporting 5% by weight of cerium oxide and 2% by weight of vanadium oxide.

The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 4.

## Reference Example 4.

15 ml of  $\alpha$ -alumina of Example 12 was immersed for an hour in 15 ml of aqueous solution of vanadyl oxalate prepared by dissolving 2.7 g of vanadium pentoxide and 6.3 g of oxalic acid and the product was dried and calcined in accordance with the process of Example 12 to yield a catalyst of  $\alpha$ -alumina supporting 5% by weight of vanadium oxide.

The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 4.

## Example 13.

15 ml of silica was immersed in 15 ml of an aqueous solution of 2.3 g of cerium nitrate for 1 hour and the product was dried and calcined in accordance with the process of Example 10 to yield 15 ml of silica supporting cerium oxide.

The 15 ml of silica supporting cerium oxide was immersed for an hour in 15 ml of aqueous solution of vanadyl oxalate prepared by dissolving 0.92 g of vanadium pentoxide and 2.1 g of oxalic acid and filtered and the product was dried and calcined in accordance with the process of Example 10, to yield a catalyst of silica supporting 5% by weight of cerium oxide and 5% by weight of vanadium oxide.

The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 4.

## Reference Example 5.

15 ml of silica of Example 13 was immersed in 15 ml of an aqueous solution of 4.4 g of cerium nitrate for 3 hours and the product was dried and calcined in accordance with the process of Example 10 to yield a catalyst of silica supporting 9% by weight of cerium oxide.

The results of  $NO_x$  decomposing tests using the catalyst are shown in Table 4.



## Reference Example 6.

15 ml of silica of Example 13 was immersed  
 in 15 ml of an aqueous solution of vanadyl  
 oxalate, and the product was dried and calcined  
 in accordance with the process of Example 13

to yield a catalyst of silica supporting 5% by  
 weight of vanadium oxide.

The results of NO<sub>x</sub> decomposing tests using  
 the catalyst are shown in Table 4.

TABLE 4

	Amount of V <sub>2</sub> O <sub>5</sub> supported (wt. %)	Amount of Catalyst (g)	Reaction temperature (°C)	NO <sub>x</sub> removal ratio (%)
Example 10	10	7.1	200	57
			250	75
			300	86
			340	91
			380	92.5
			400	93
			420	93
			460	89
			490	77
Example 11	5	7.1	200	54
			250	71
			300	83
			340	88
			380	90.5
			400	91
			420	91.5
			460	91.5
			500	88.5
			520	85
			540	77
Example 12	2	11.5	250	66
			300	81
			340	86.5
			380	89
			400	89.5
			420	88.5
			440	85.5
			460	77

TABLE 4 (continued)

	Amount of V <sub>2</sub> O <sub>5</sub> supported (wt. %)	Amount of Catalyst (g)	Reaction temperature (°C)	NO <sub>x</sub> removal ratio (%)
Reference Example 4	5	12.6	260	66
			300	77
			340	83.5
			360	84.5
			380	85
			400	81.5
			420	73
Example 13	5	4.8	250	45
			300	57
			340	62
			360	62
			380	60.5
			400	58
			420	53
Reference Example 5	9	4.8	250	16.1
			310	34.9
			335	25.9
Reference Example 6	5	4.8	300	19
			320	20
			340	20.5
			360	18
			380	12

## Example 14.

5 An  $\alpha$ -alumina honeycomb-coated with  $\gamma$ -alumina having diameter of 17 mm and length of 25 mm was immersed for 6 hours in an aqueous solution of vanadyl oxalate prepared by dissolving 3.426 g of vanadium pentoxide in 7.88 g of oxalic acid and 10 ml of water.

10 The solution was filtered and the product was dried and calcined at 250° C for 1 hour, at 350° C for 1 hour and at 550° C for 3 hours in nitrogen atmosphere, to yield a honeycomb type catalyst of  $\alpha$ -alumina coated with  $\gamma$ -alumina supporting 6% by weight of vanadium oxide.

The results of NO<sub>2</sub> decomposing tests using the catalyst are shown in Table 5.

## Reference Example 7.

20 An  $\alpha$ -alumina honeycomb was immersed for 6 hours in 10 ml of aqueous solution of vanadyl oxalate prepared by dissolving 3.616 g of vanadyl pentoxide in 8.32 g of oxalic acid and 10 ml of water and the product was dried and calcined in accordance with the process of Example 14 to yield a honeycomb type catalyst of  $\alpha$ -alumina supporting 6% by weight of vanadium oxide.

25 The results of NO<sub>2</sub> decomposing tests using

the catalyst are shown in Table 5.

#### Example 15.

A honeycomb type mullite was immersed in a slurry of  $\gamma$ -alumina, and dried and calcined to yield a carrier. The carrier was immersed for 6 hours in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 2.405 g of vanadium pentoxide in 5.53 g of oxalic acid and 10 ml of water. The solution was filtered and the product was dried and calcined in accordance with the process of Example 14 to yield a honeycomb type catalyst of mullite coated with  $\gamma$ -alumina supporting 6% by weight of vanadium oxide.

The results of  $\text{NO}_x$  decomposing tests using the catalyst are shown in Table 5.

#### Reference Example 8.

A honeycomb type mullite was immersed in an aqueous solution of vanadyl oxalate prepared by dissolving 2.267 g of vanadium

pentoxide in 5.214 g of oxalic acid and 10 ml of water. The product was dried and calcined in accordance with the process of Example 14 to yield a honeycomb type catalyst of mullite supporting 10% by weight of vanadium oxide.

The results of  $\text{NO}_x$  decomposing tests using the catalyst are shown in Table 5.

#### Example 16.

A honeycomb type cordierite coated with  $\gamma$ -alumina was immersed for 6 hours in 10 ml of an aqueous solution of vanadyl oxalate prepared by dissolving 2.398 g of vanadium pentoxide in 5.52 g of oxalic acid and 10 ml of water and the product was dried and calcined in accordance with the process of Example 14 to yield a honeycomb type catalyst of cordierite coated with  $\gamma$ -alumina supporting 6% by weight of vanadium oxide.

The results of  $\text{NO}_x$  decomposing tests using the catalyst are shown in Table 5.

TABLE 5

	Amount of $\text{V}_2\text{O}_5$ supported (wt. %)	Amount of Catalyst (g)	Reaction temperature ( $^{\circ}\text{C}$ )	$\text{NO}_x$ removal ratio (%)
Example 14	6	5.8	200	44
			260	79
			300	91.3
			350	94.8
			380	86
Reference Example 7	6	5.6	250	24.3
			330	33.5
			380	36.5
			400	35
Example 15	6	5.9	220	61.8
			280	90
			340	97
			380	94.8
Reference Example 8	10	1.6	250	26.5
			310	46.5
			370	58.5
			390	57

TABLE 5 (Continued)

	Amount of V <sub>2</sub> O <sub>5</sub> supported (wt. %)	Amount of Catalyst (g)	Reaction temperature (°C)	NO <sub>x</sub> removal ratio (%)
Example 16	6	5.5	210	45.5
			270	80
			340	95.8
			360	95

## WHAT WE CLAIM IS:—

1. A process for the reductive decomposition of oxides of nitrogen contained in a gas which comprises treating the gas with ammonia in the presence of a catalyst comprising as active ingredients vanadium oxide supported on a carrier formed at least externally of titanium oxide, zirconium oxide, cerium oxide,  $\gamma$ -alumina, or a mixture of two or more thereof.
2. A process as claimed in claim 1 wherein the catalyst comprises vanadium oxide supported on a carrier formed of titanium oxide, zirconium oxide or a mixture thereof.
3. A process as claimed in claim 1 wherein the catalyst comprises vanadium oxide supported on a carrier formed of a heat resistant substance coated with titanium oxide.
4. A process as claimed in claim 1 wherein the catalyst comprises vanadium oxide supported on a carrier formed of a heat resistant substance coated with cerium oxide.
5. A process as claimed in claim 1 wherein the catalyst comprises vanadium oxide supported on a carrier formed of a heat resistant substance coated with  $\gamma$ -alumina.
6. A process as claimed in claim 1 wherein the catalyst comprises vanadium oxide supported on a carrier formed of a heat resistant substance coated with a mixture of titanium oxide and  $\gamma$ -alumina.
7. A process as claimed in any of claims 3 to 6 wherein the heat resistant substance comprises alumina, silica-alumina, diatomaceous earth, silicon carbide, mullite or cordierite.
8. A process as claimed in claim 7 wherein

the heat resistant substance comprises  $\alpha$ -alumina.

9. A process as claimed in any preceding claim wherein the catalyst is prepared by dipping the carrier in an aqueous solution of a vanadium compound and calcinating it at 400—700° C.

10. A process as claimed in any of claims 1 to 8 wherein the catalyst is prepared by dipping a heat resistant carrier substance coated with titanium oxide, cerium oxide or  $\gamma$ -alumina in an aqueous solution of a vanadium compound and calcinating it at 400—700° C.

11. A process as claimed in any preceding claim in which the catalyst contains 0.1—50% by weight of vanadium oxide based on the total weight of the catalyst.

12. A process as claimed in any preceding claim wherein the gas and ammonia are contacted with the catalyst at 150—650° C.

13. A process as claimed in any preceding claim wherein the mixture of ammonia and the gas containing oxides of nitrogen is passed through a zone containing the catalyst at a space velocity of 1,000—150,000 hr<sup>-1</sup>.

14. A process as claimed in claim 1 substantially as described herein with reference to any one of the Examples.

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